A Study of the Decay Rates of Ethyl-Methyl Parathion and Endosulfan Applied as a Foliar Spray to a Tomato Field in the Sacramento Valley of California

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As a part of a study of potential field worker safety hazards, an analysis was made of the rate of decay of ethyl-methyl parathion and endosulfan (Tiovel) applied as a foliar spray to a tomato crop in the Sacramento Valley of California.

On July 20, 1976, a 340 acre tomato field in Yolo County was treated aerially with the following formulation per acre:

0.5 pt	Ortho parathion-methyl parathion, 6-3 emulsive
2 qt	Tiovel (endosulfan)
2 qt	Difolatan
0.1 qt	No Foam
10 gal	Water

Sampling was done by taking 100 leaf punches on a diagonal from random rows across the field for each of three samples. Duplicate samples were taken for surface and penetrated analysis, and the third for total residue. Results for the first two were averaged. Application was completed shortly before noon and the first field sample was collected at 2 p.m. that afternoon. The subsequent three samples were taken in the late morning on the following three days. The rates of degradation of ethyl parathion, methyl parathion, and endosulfan were monitored.

Results: Results of the degradation study of ethyl and methyl parathion and Tiovel (endosulfan) are shown in table one and in the following graphs. The residues of methyl parathion, and its metabolites degrade to a level of less than 1.0 ppm within three days after application. The total level of ethyl parathion reduces to below 10 ppm within three days. Surface and penetrated residues of both parathion homologues decrease at comparable rates. Endosulfan exhibits quite a different pattern of degradation. Surface levels degraded approximately ten-fold in three days. This is comparable to the rates observed for parathion. Penetrated residues of endosulfan, however, degraded only slightly in the three-day test period. Thus the total residues degrade slowly.

The tolerance level of the combined parathion homologes is 1 ppm on tomatoes for human consumption. It is 2 ppm for endosulfan. Normally, however, residues are far lower in the tomato than on the foliage due to the large difference in surface-to-volume ratio. Since worker contact with foliage is not high in machine harvesting, there is usually less danger for exposure to pesticides on tomatoes than some other crops. However several thousand acres of tomatoes in California are still hand harvested each year.

Worker Reentry:

The field worker reentry safety interval for methyl parathion on tomatoes is 14 days if more than one pound per acre of actual methyl parathion is used. If less than that amount is used, no safety interval is required. The safety interval for ethyl parathion is also 14 days for the same application rates. Endosulfan has no required safety interval. Whenever a mixture of two or more organophosphate pesticides having a safety interval is applied, the safety interval is prolonged by adding to the longest applicable safety interval either (1) 50 percent of the next shortest applicable safety interval,

or (2) 4 days, whichever is the longest. Since both ethyl and methyl parathion were used together, the required safety interval would have been 21 days had more than one pound of either ethyl or methyl parathion been used. During a safety interval workers may not enter the field to engage in any activity that involves substantial and prolonged body contact with the treated plants, without medical supervision.

In this application, no safety interval was required because the use rates of neither ethyl nor methyl parathion exceeded one pound per acre.

Degradation:

Parathion (ethyl and methyl) breaks down into paraoxon, an even more highly toxic compound than the parent material. The oxon increases in concentration during the initial period of parathion degradation, then decreases.

Endosulfan I and endosulfan II are both found in the product before application. Endosulfan I, however, is in much greater abundance than its isomer, endosulfan II. Upon exposure to the elements, the parent compound immediately begins isomerization so that approximately equivalent amounts are found in residues. Endosulfan III is a degradation product of both endosulfan I and II. Its toxicity is lower than the parent compounds.

Analytical Procedures:

Extraction

The procedure used for the extraction of dislodgeable, penetrated, and total residues from leaf punches was originally published by Gunther in "The Bulletin of Environmental Contamination and Toxicology", 9, 243-249, 1973. It has been documented several times in detail, with modifications that were made to accommodate the various pesticides and their metabolites. The sample container and leaf punches are weighed and the gross weight recorded.

Total Residues

1. The leaf punches are transferred to a blending jar. The empty sample container is again weighed and the net weight of the punches recorded.

2. Approximately 50 gm of sodium sulfate and 100 ml of organic solvent (ethyl acetate) are added.

3. The sample is blended at high speed for 3 minutes, keeping the blender cup cool by immersing it in a container of cool water. The blender cup is removed and the sample allowed to settle.

4. An aliquot is decanted into a Teflon-capped bottle and may be stored in the freezer prior to clean up and analysis.

Dislodgeable Residues

1. Fifty ml of water and approximately 4 drops of sur-ten solution (1:50) is added to the sample containers. The containers are capped and placed in a multi-purpose rotator and rotated at 30 cycles/min. for 60 min. The aqueous solution is decanted through a glass wool plug into a 500 ml separatory funnel.

2. The punches are rotated a second time, using 50 ml of water and 4 drops of sur-ten solution for 30 min. This is added to the first extraction.

3. The sample is then hand shaken for approximately 10 seconds with 30 ml of water. The container is drained into the separatory funnel with the first two extractions.

4. The aqueous solution is extracted three times with 50 ml of organic solvent. The solvent is filtered through sodium sulfate into a glass stoppered mixing cylinder and the volume is recorded. The solvent is mixed in the cylinder. An aliquot is decanted into a Teflon-capped bottle and stored in the freezer prior to cleanup and analysis.

Penetrated Residues

1. After the last water rinse is drained for the dislodgeable residue, the punches are transferred to a blender jar. The empty sample container is weighed and the net weight of the punches recorded.

2. Approximately 50 gm of sodium sulfate and 100 ml of solvent are added.

3. The sample is blended and handled the same as the total residue sample.

Gas Chromatography

Parathion

The gas chromatograph used was a Tracor Model 500 operated under the following conditions:

Flame photometric detector: 250°C
Detector gas flow rates: H_2 - 100 ml/min.
Air - 80 ml/min.
Column: 6.0' x 2 mm I.D. of 3& OV-10 on 100.120
Gas Chrom Q: 185°C
Carrier gas: N_2 30 ml/min.

Quantitation of parathion and oxone residue was accomplished by comparision of standard and sample peak heights, which were matched to within $\pm$ 10%.

Endosulfan

The gas chromatograph used was a Tracor Model 550GC operated under the following conditions:

Column Temp: 180°C
Carrier Gas: N_2 - 70 ml/min.
Attenuation: 16 x 10^2 med.
Column: 6' x 2 mm GEXE 60
Detector: Electron Capture (Ni^{63})

Table I

Methyl Parathion

Sample Date	Surface Residue (PPM) M-Parathion	M-Paraoxon	Penetrated Residue (PPM) M-Parathion	M-Paraoxon	Total Residue (PPM) M-Parathion	M-Paraoxon
7/20	14.25	--	9.8	--	21.5	--
7/21	8.88	0.23	3.26	0.32	10.0	0.58
7/22	3.79	--	1.47	0.25	3.46	0.32
7/23	0.60	--	0.87	0.22	0.79	0.19

Ethyl Parathion

Sample Date	Surface Residue (PPM) E-Parathion	E-Paraoxon	Penetrated Residue (PPM) E-Parathion	E-Paraoxon	Total Residue (PPM) E-Parathion	E-Paraoxon
7/20	2.25	0.32	33.2	0.54	56.4	1.18
7/21	12.2	0.60	20.15	1.65	30.4	2.37
7/22	6.1	0.62	11.65	3.32	20.0	2.44
7/23	2.68	0.32	5.83	1.58	6.03	1.79

Endosulfan

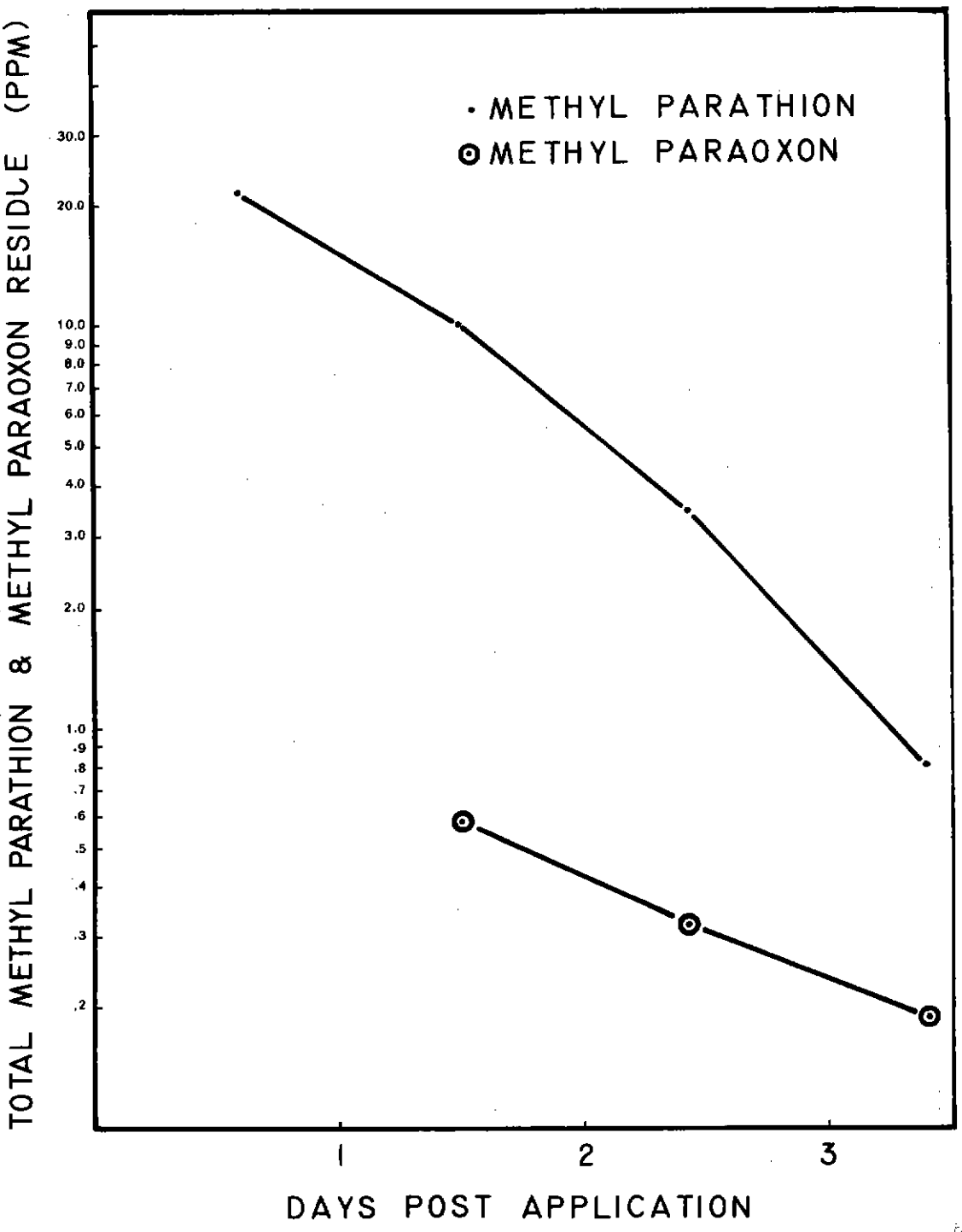
Sample Date	Surface Residue (PPM) Endosulfan I	Endosulfan II	Endosulfan III	Penetrated Residue (PPM) Endosulfan I	Endosulfan II	Endosulfan III	Total Residue (PPM) Endosulfan I	Endosulfan II	Endosulfan III
7/20	21.14	30.55	--	18.61	33.24	--	16.87	36.55	--
7/21	13.86	20.96	--	17.02	33.25	4.2	10.80	24.36	17.3
7/22	9.44	18.68	--	16.34	31.36	--	16.72	33.34	--
7/23	1.23	7.35	--	13.76	25.55	1.1	13.00	27.05	8.1

Table II

Weather Conditions for the Experimental Period

	Temp (°F) High	Low	
7/20	95	58	clear
7/21	92	58	clear
7/22	98	59	clear in a.m./ slightly cloudy in p.m.
7/23	98	66	slightly cloudy in a.m.
	$\bar{x}$=96	60	clear in p.m.

There was no precipitation during the experimental period.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⊙ METHYL PARAOXON
TOTAL METHYL PARATHION & METHYL PARAOXON RESIDUE (PPM)
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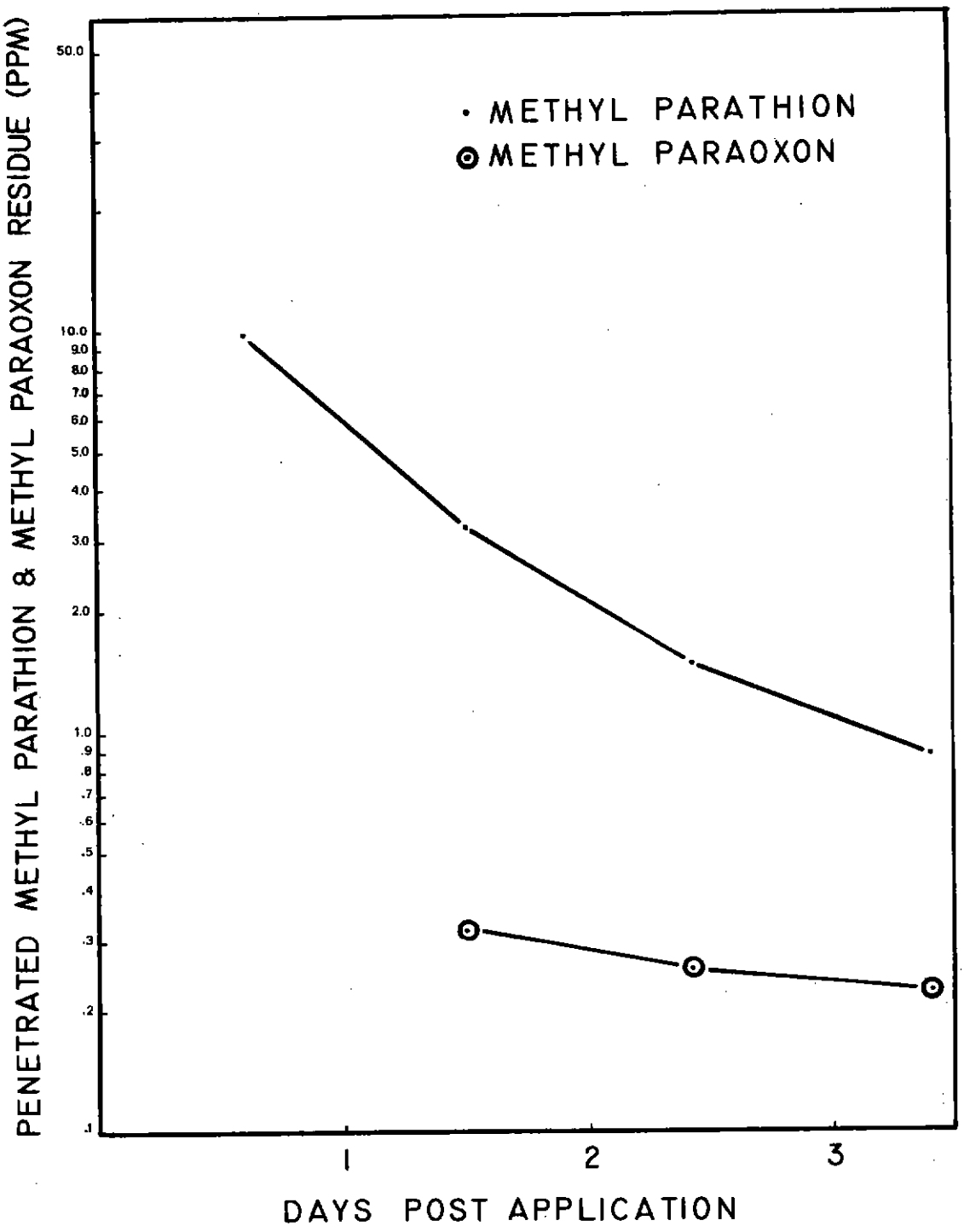
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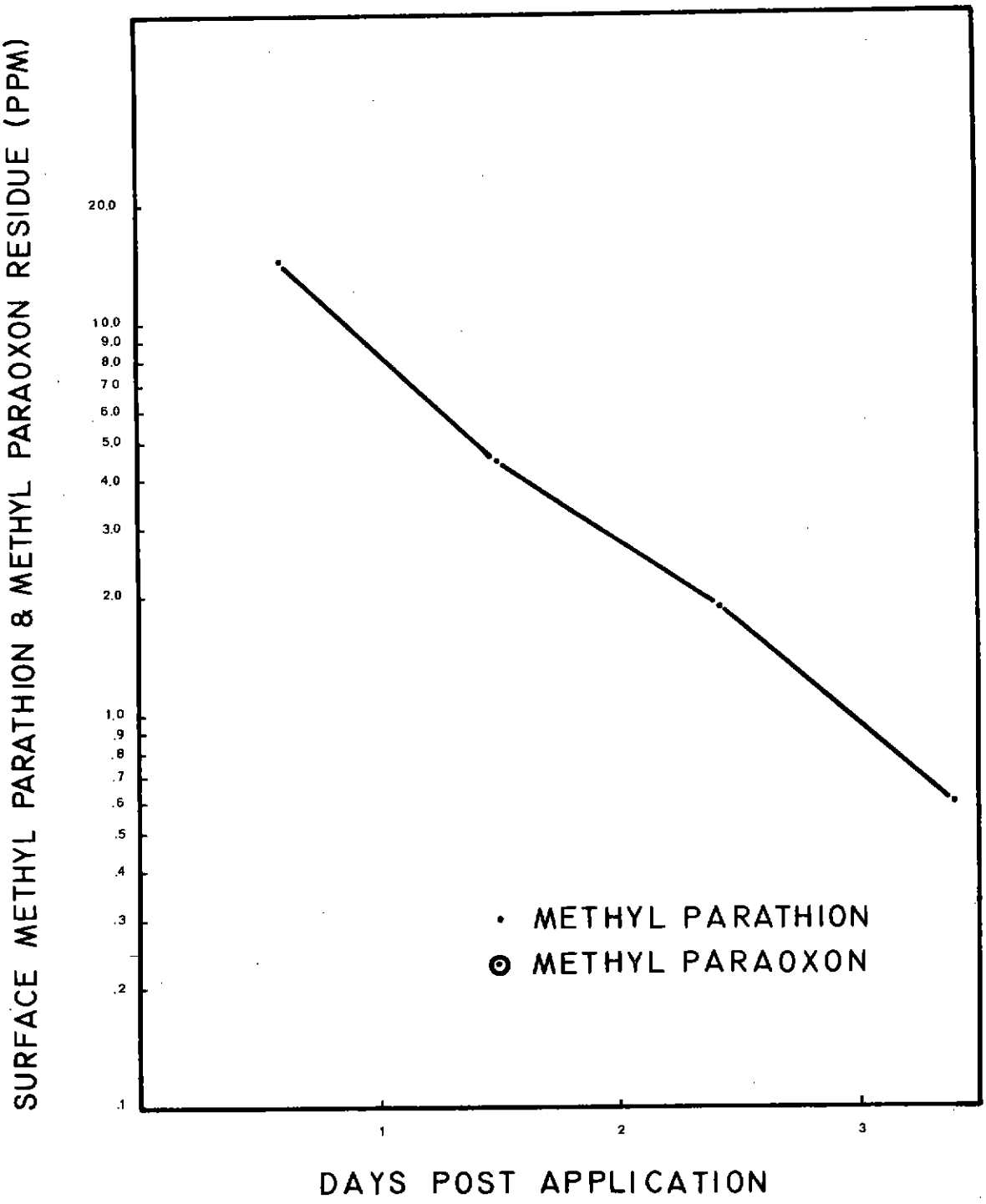
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METHYL PARATHION
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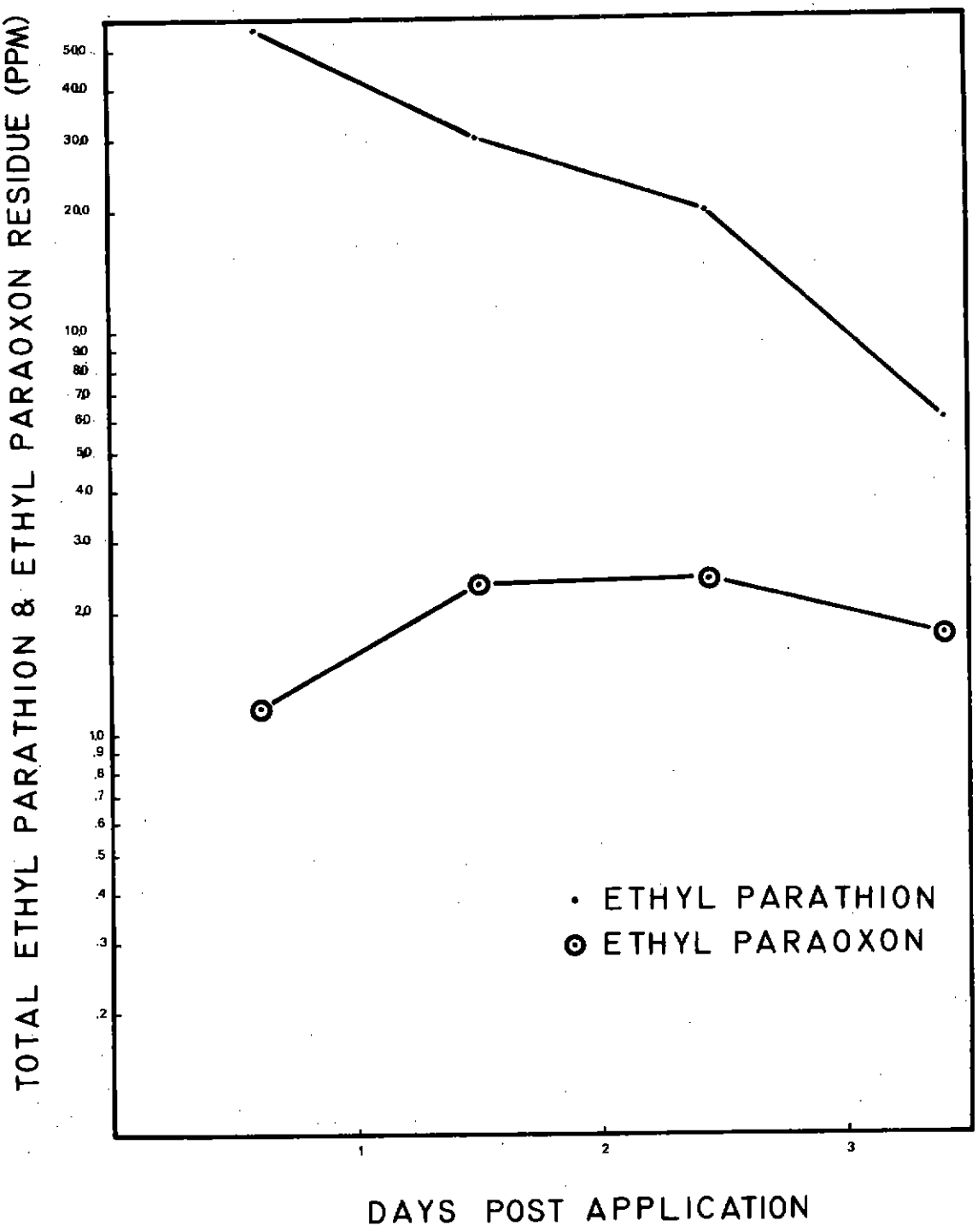
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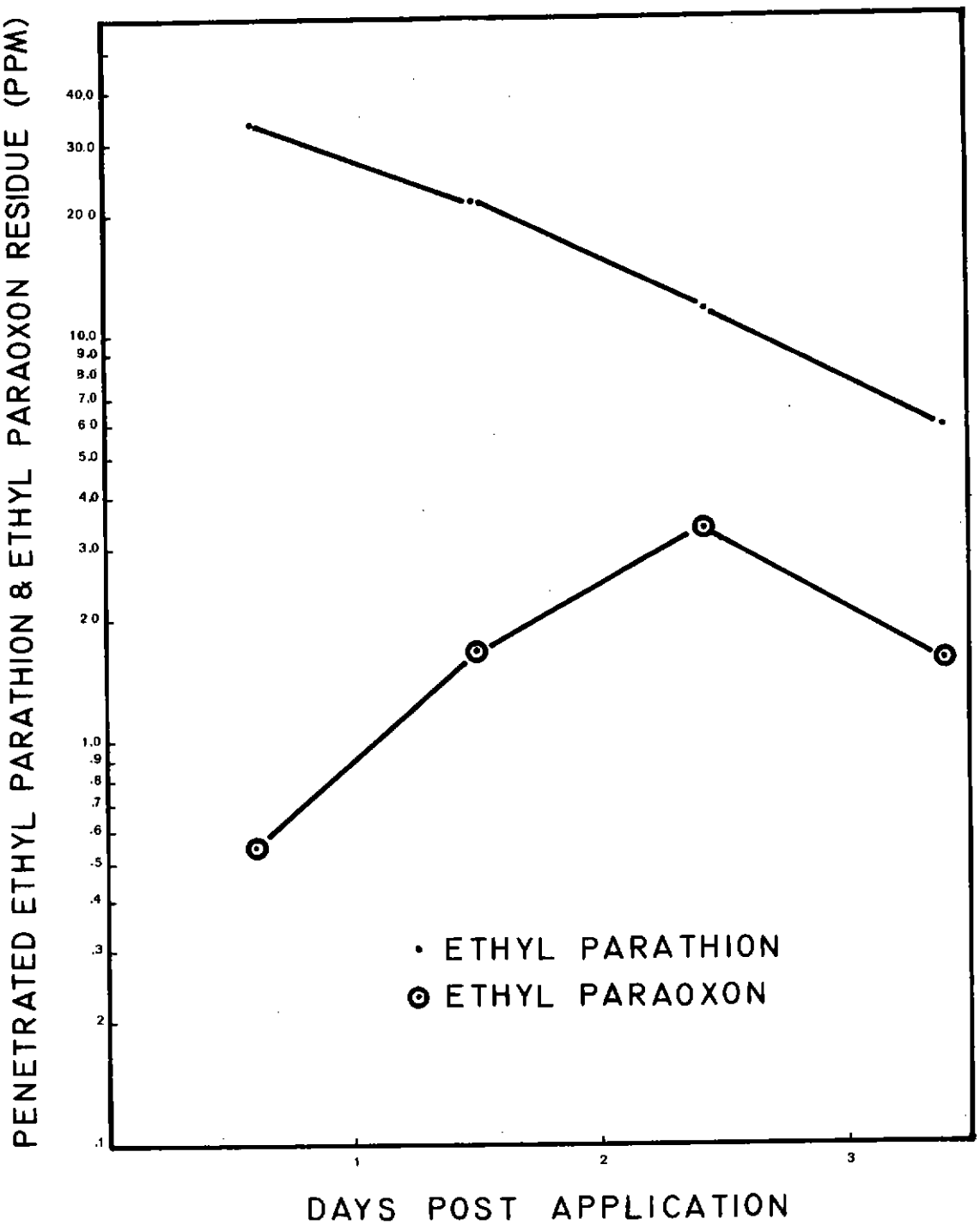
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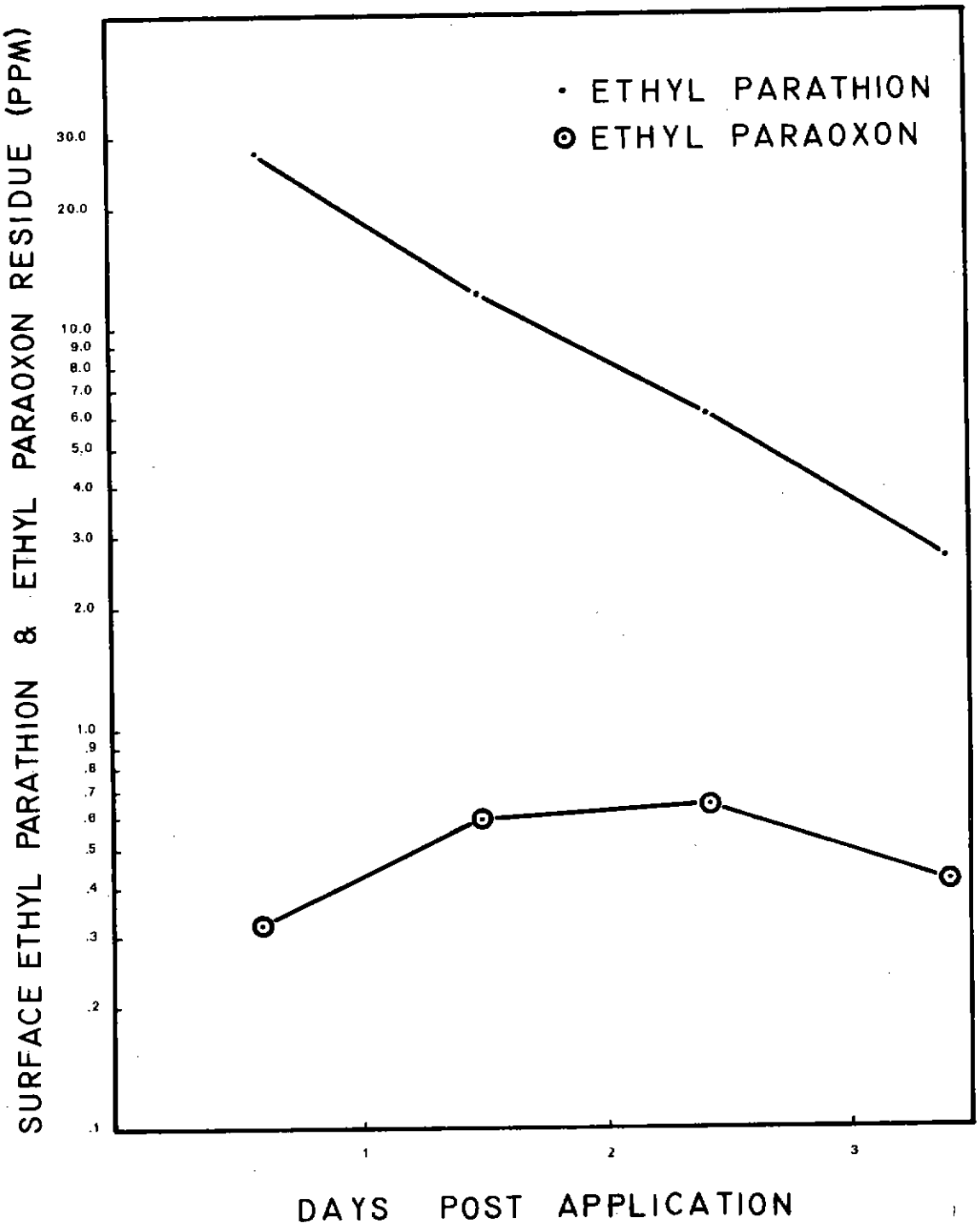
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SURFACE ETHYL PARATHION & ETHYL PARAOXON RESIDUE (PPM)
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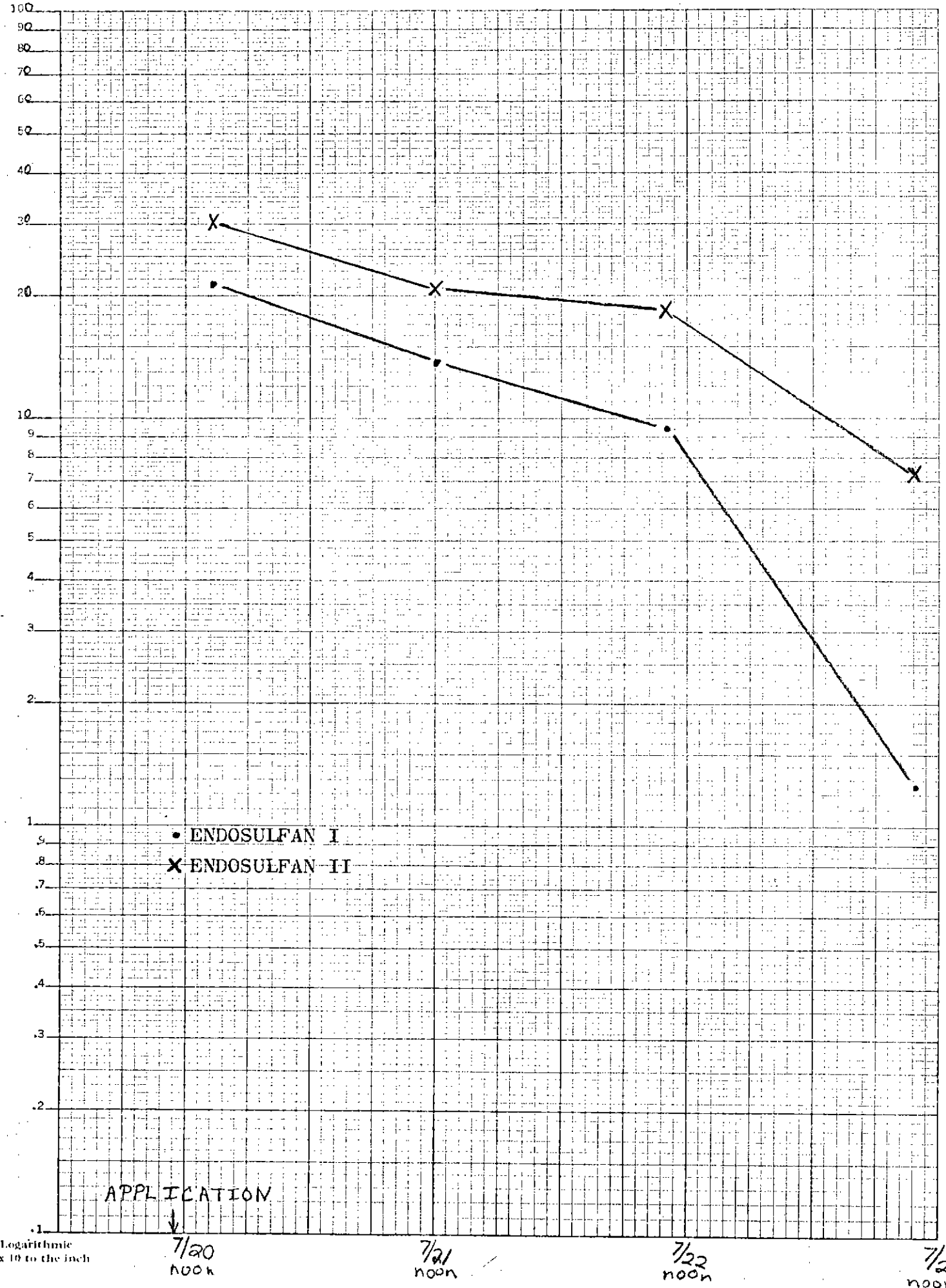
SURFACE ENDOSULFAN I + II RESIDUE (PPM)



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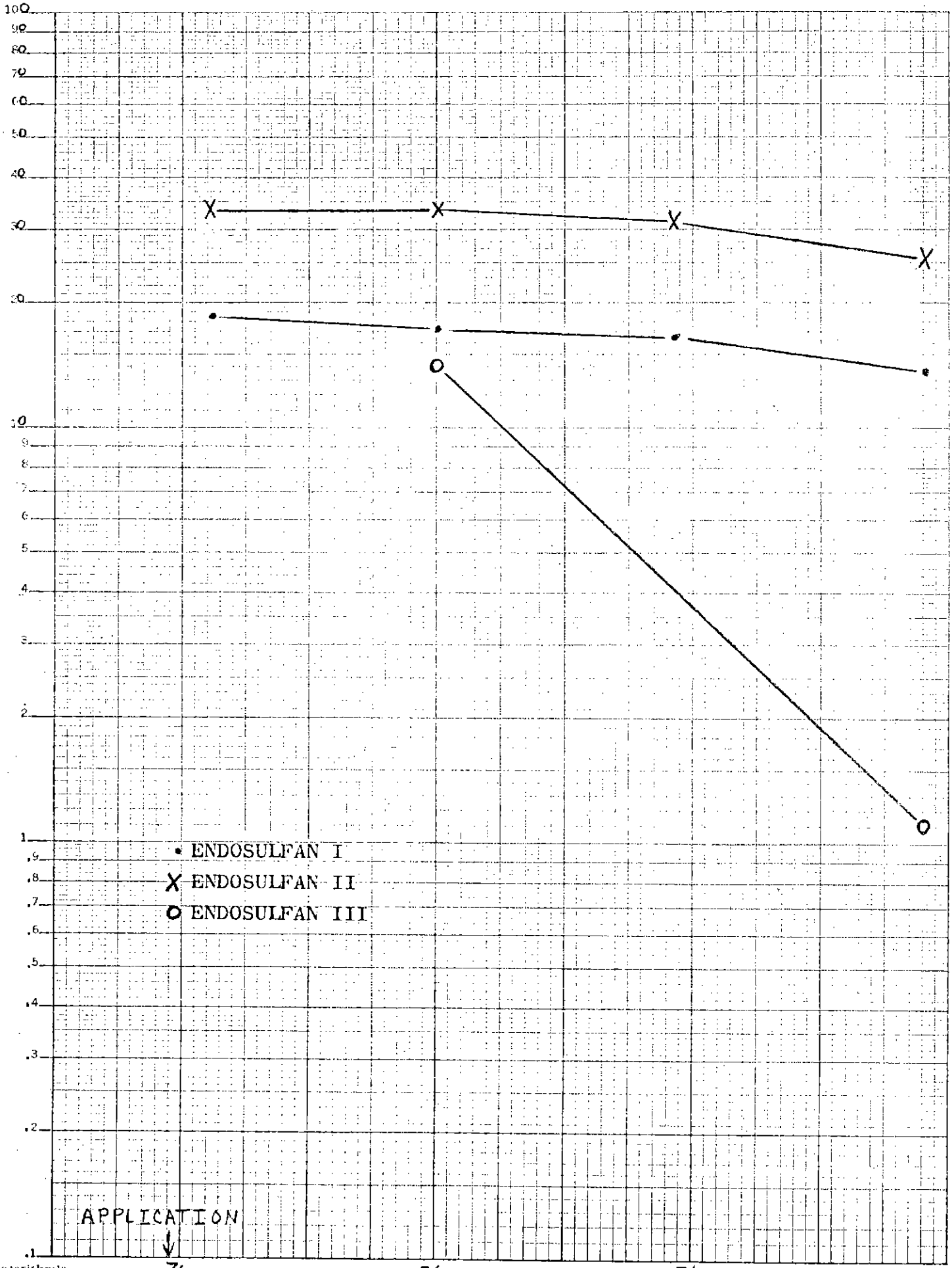
3 Cycles x 10 to the inch

PENETRATED ENDOSULFAN I, II, + III RESIDUE (PPM)



Semi-Logarithmic
3 Cycles x 10 to the inch

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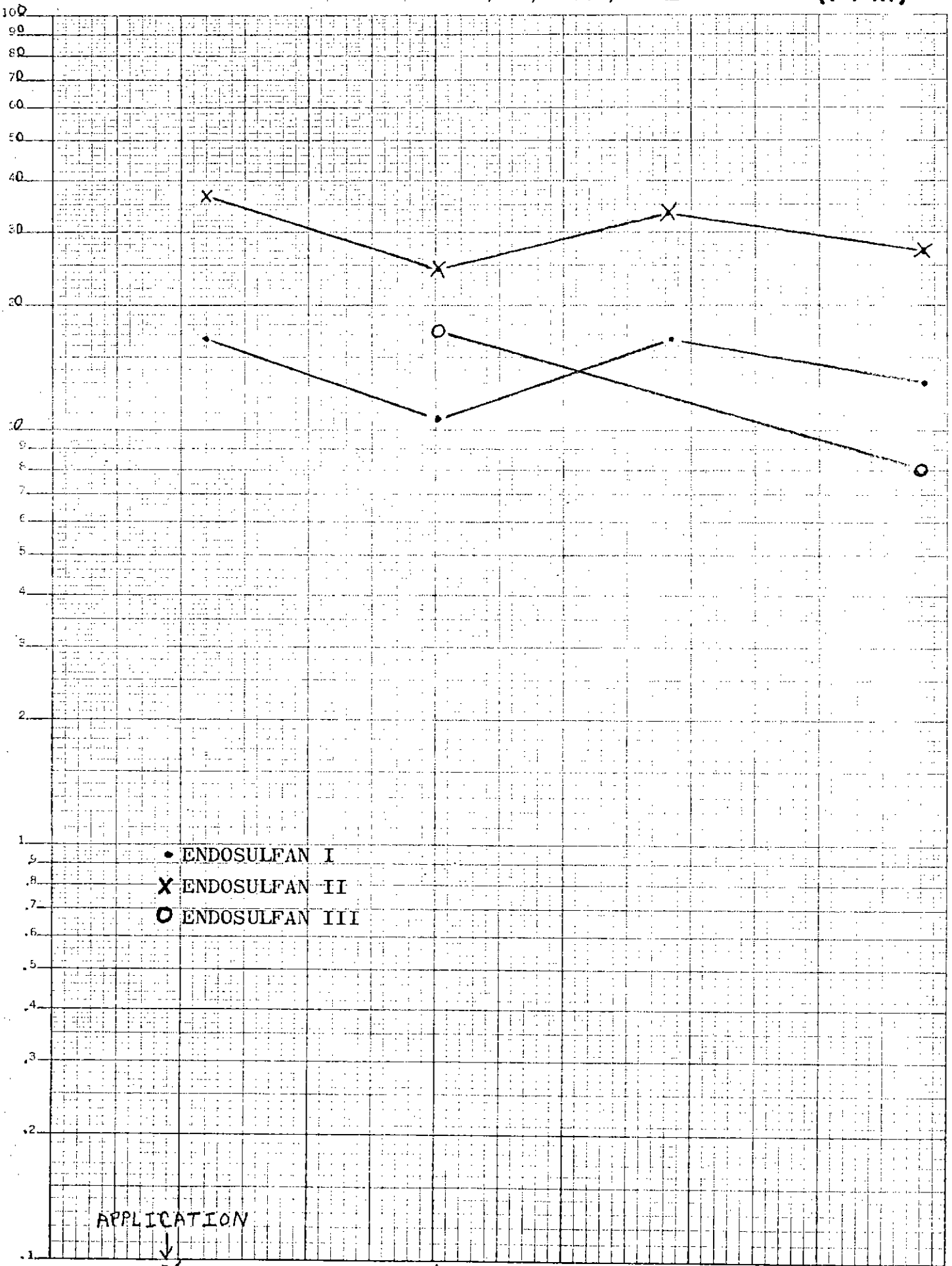

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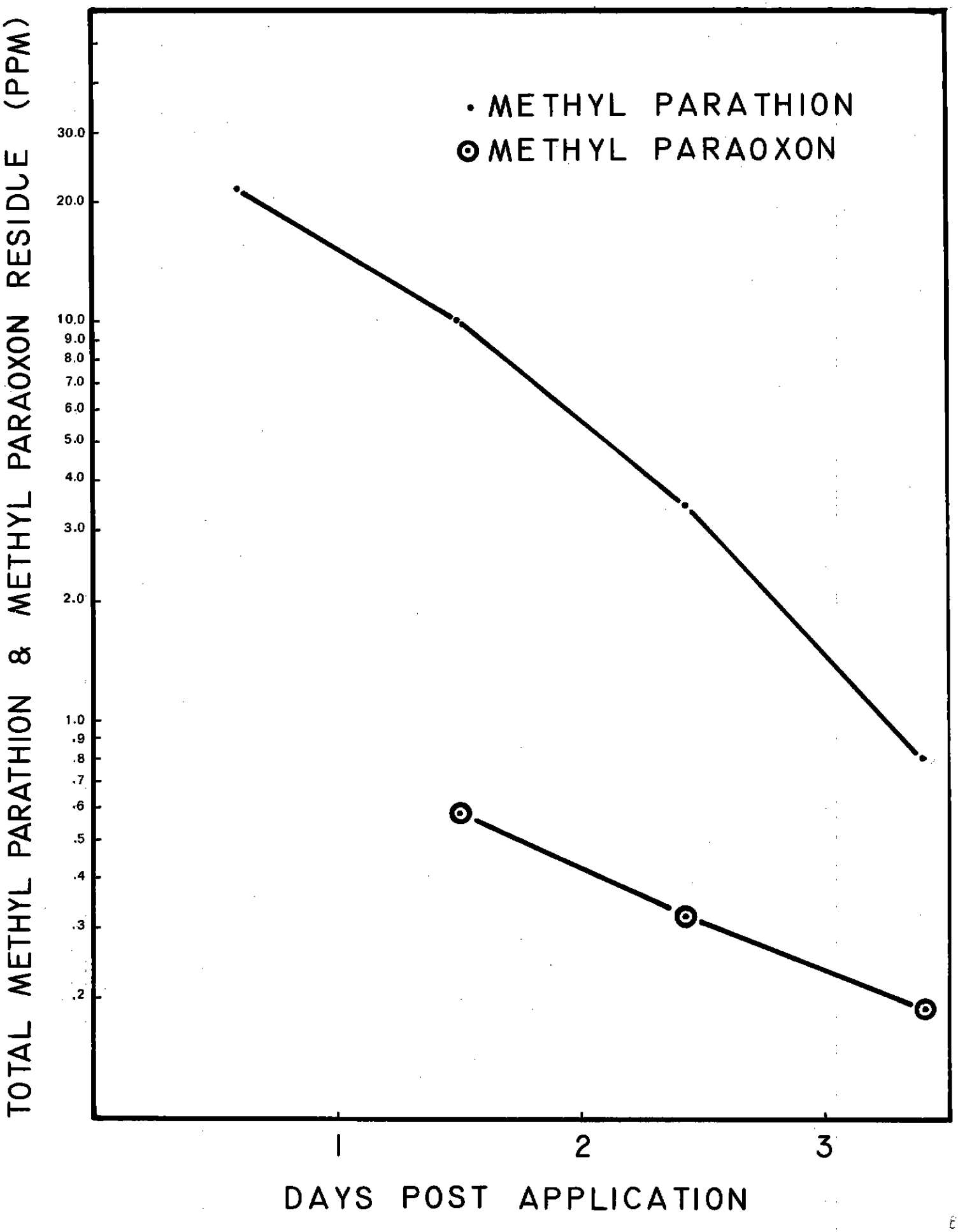
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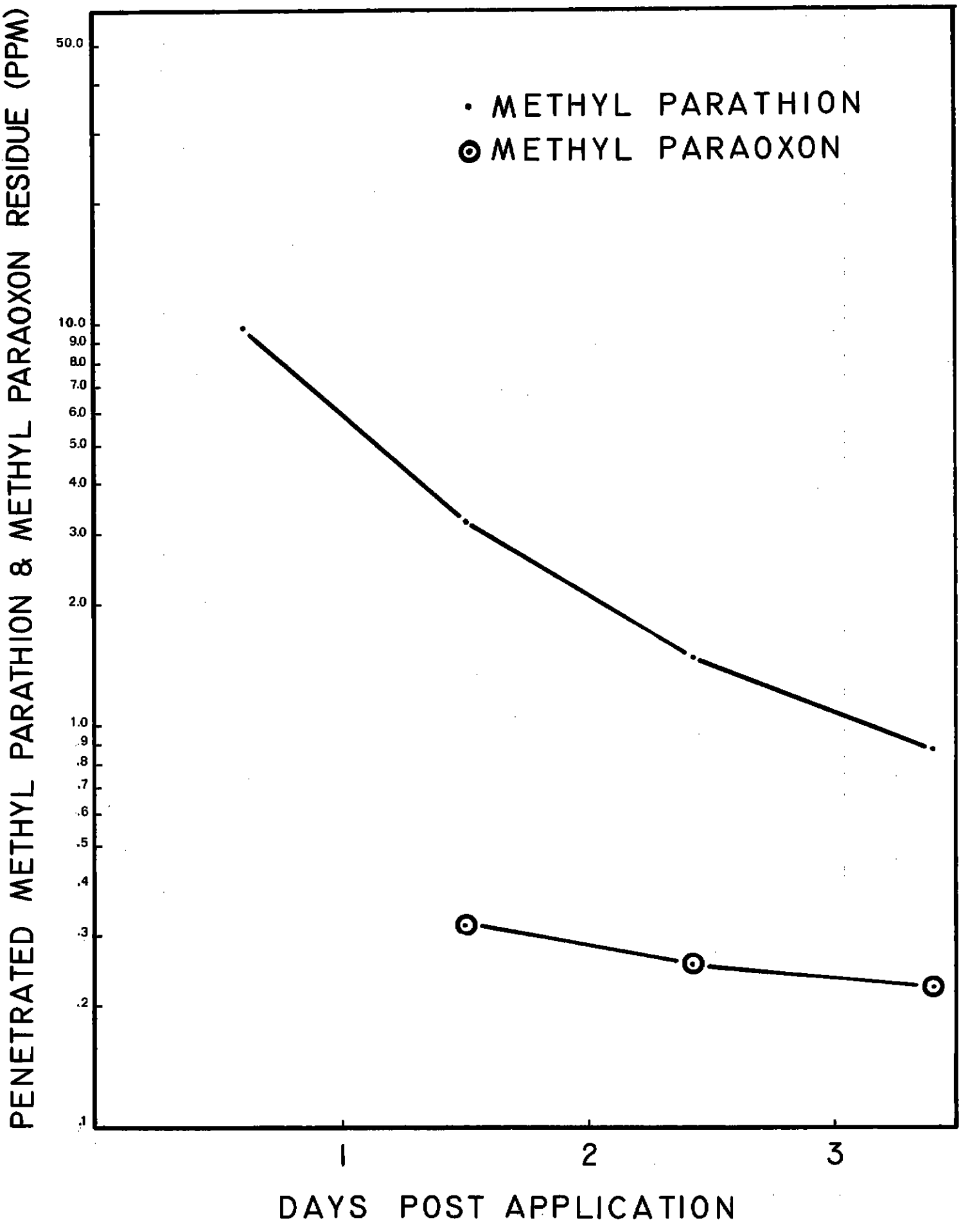
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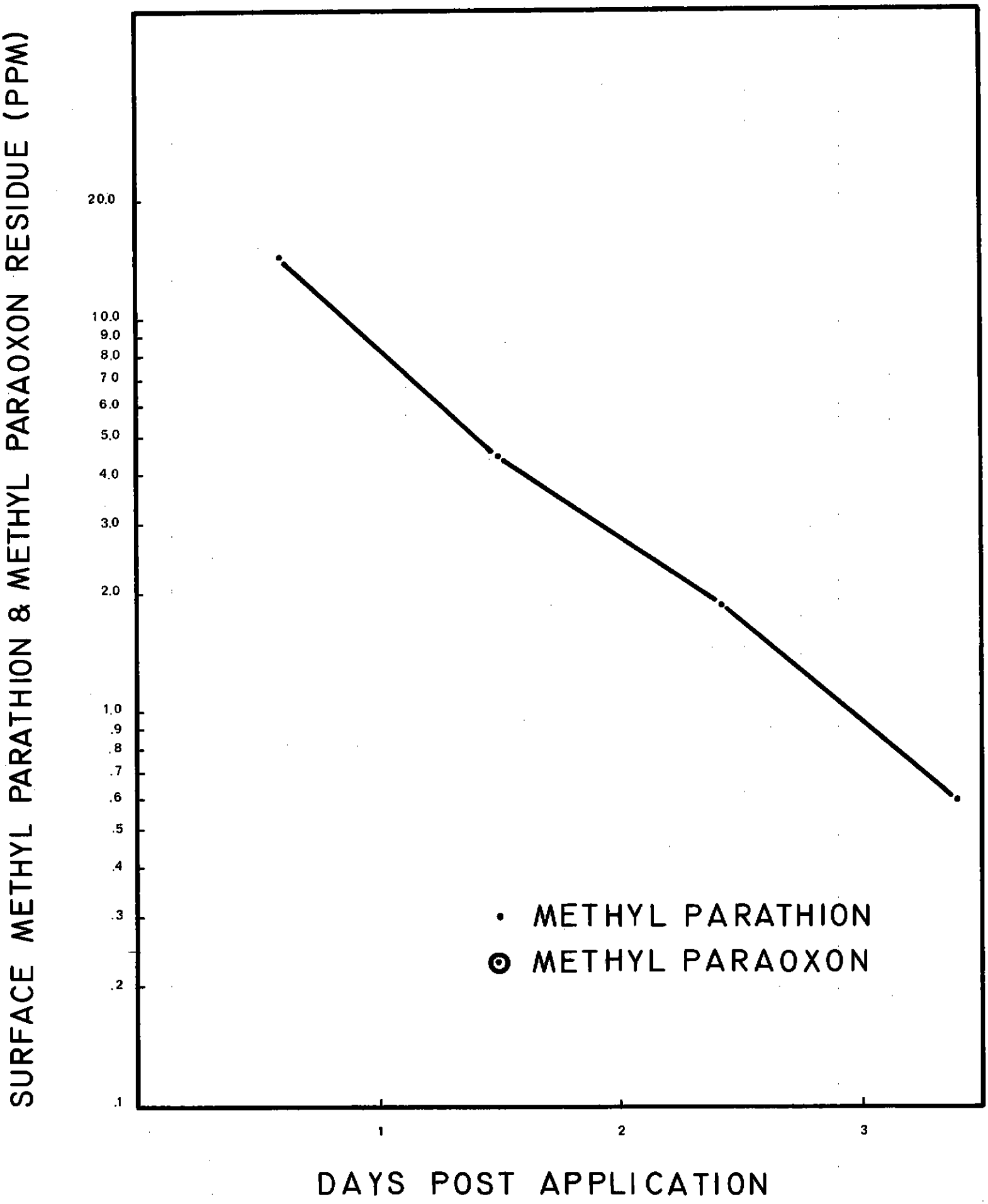
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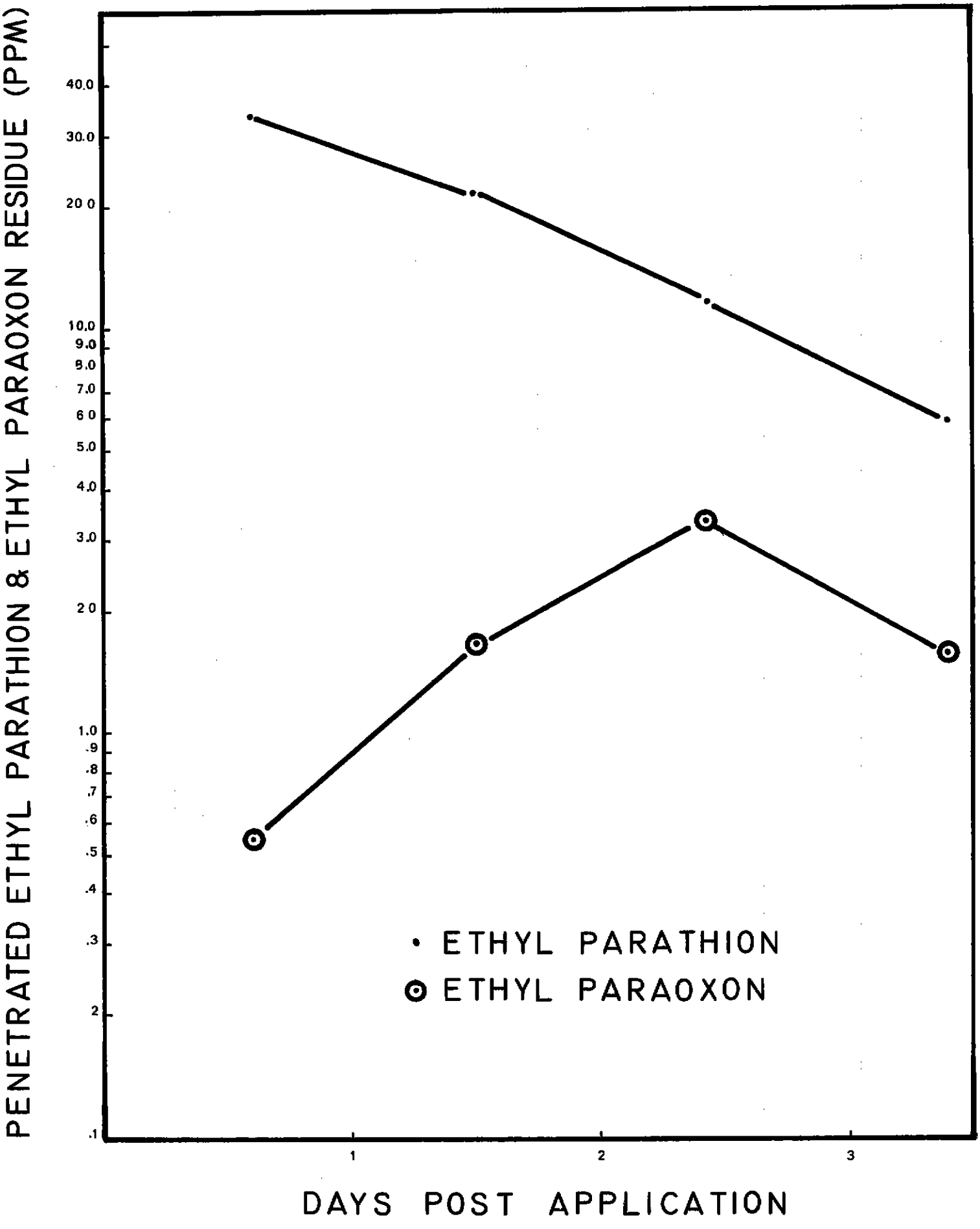
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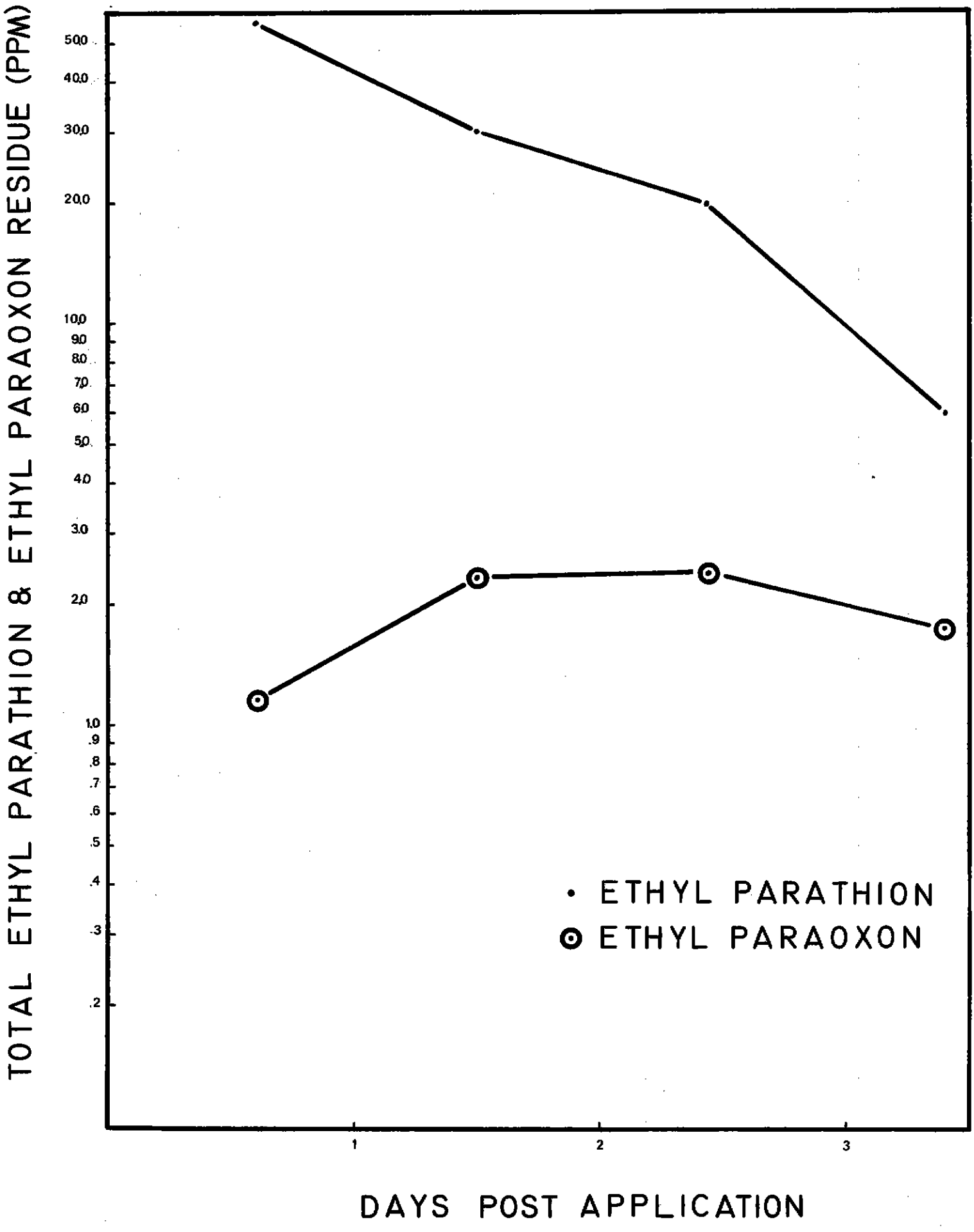
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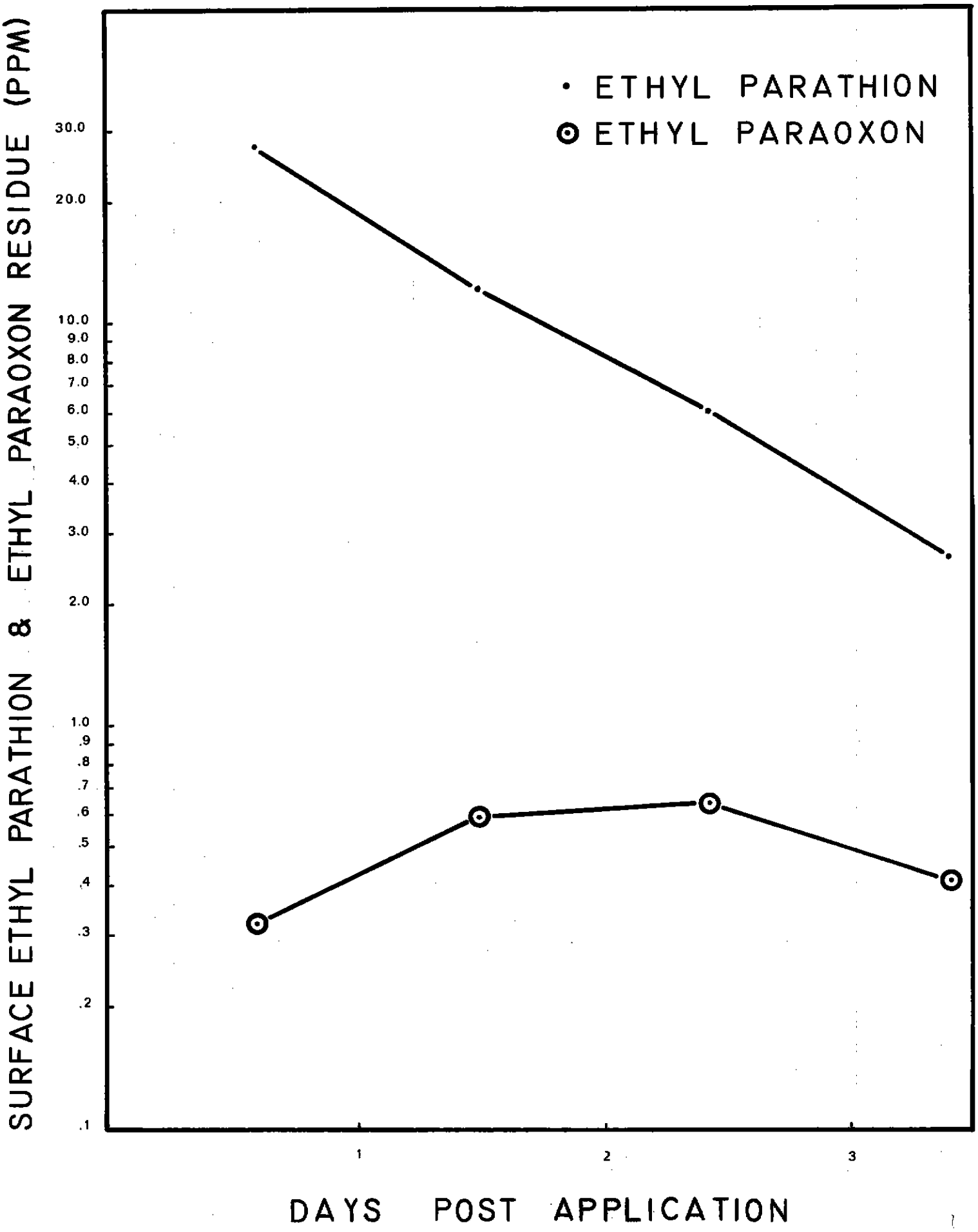
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SURFACE ETHYL PARATHION & ETHYL PARAOXON RESIDUE (PPM)
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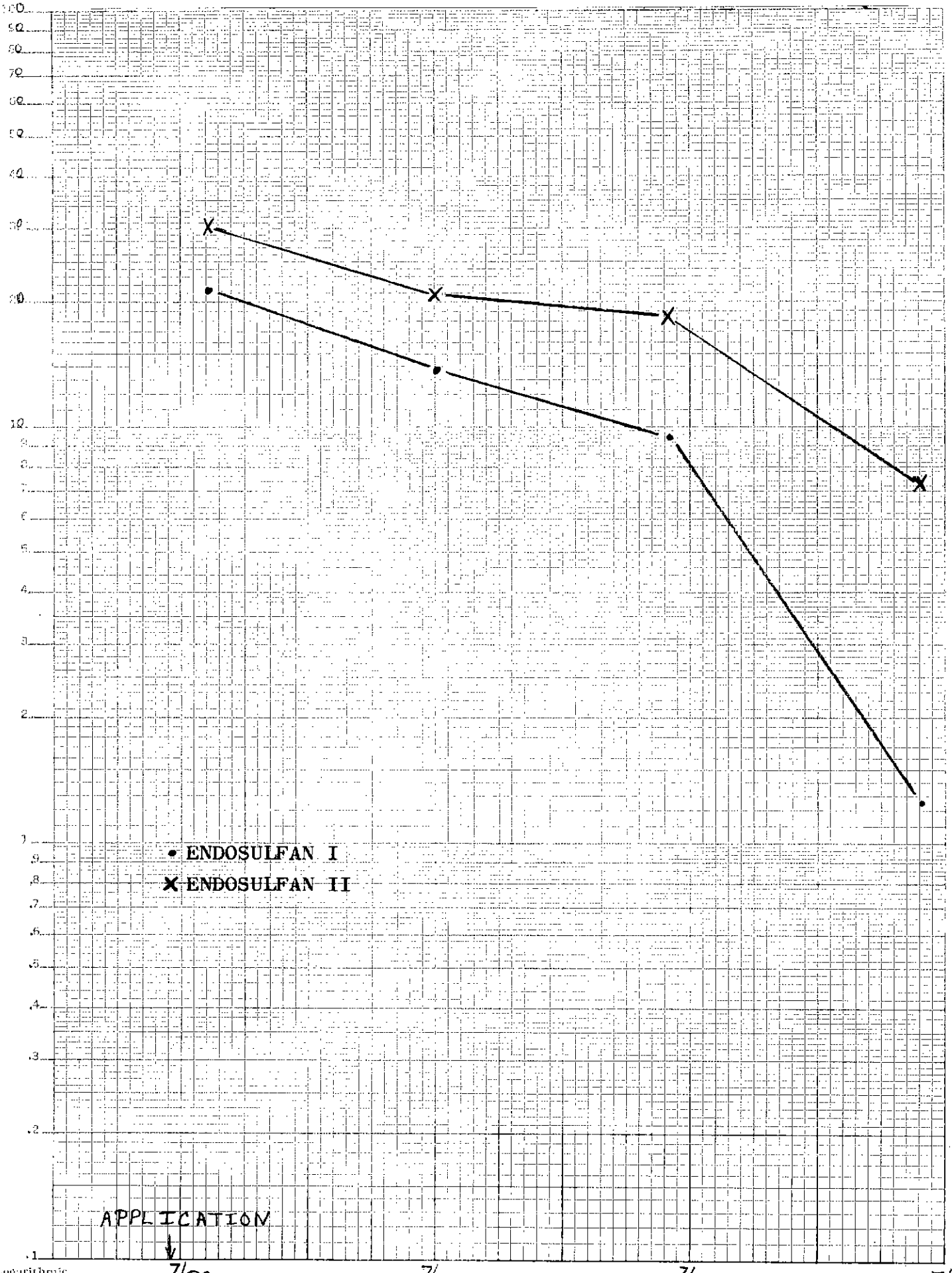
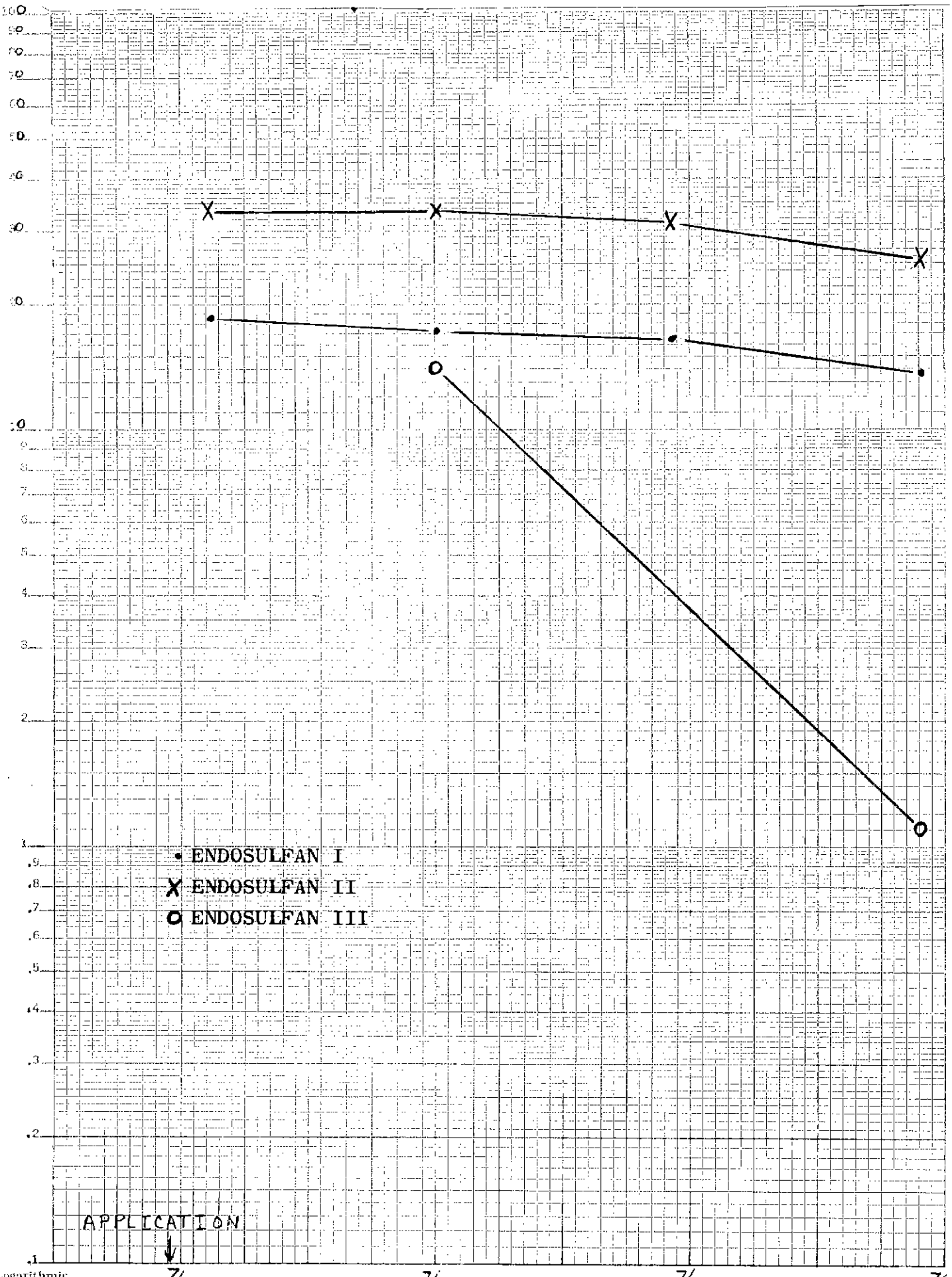
DAYS POST APPLICATION

SURFACE ENDOSULFAN I + II RESIDUE (PPM)



Semi-Logarithmic
3 Cycles x 10 to the Inch

PENETRATED ENDOSULFAN I, II, + III RESIDUE (PPM)



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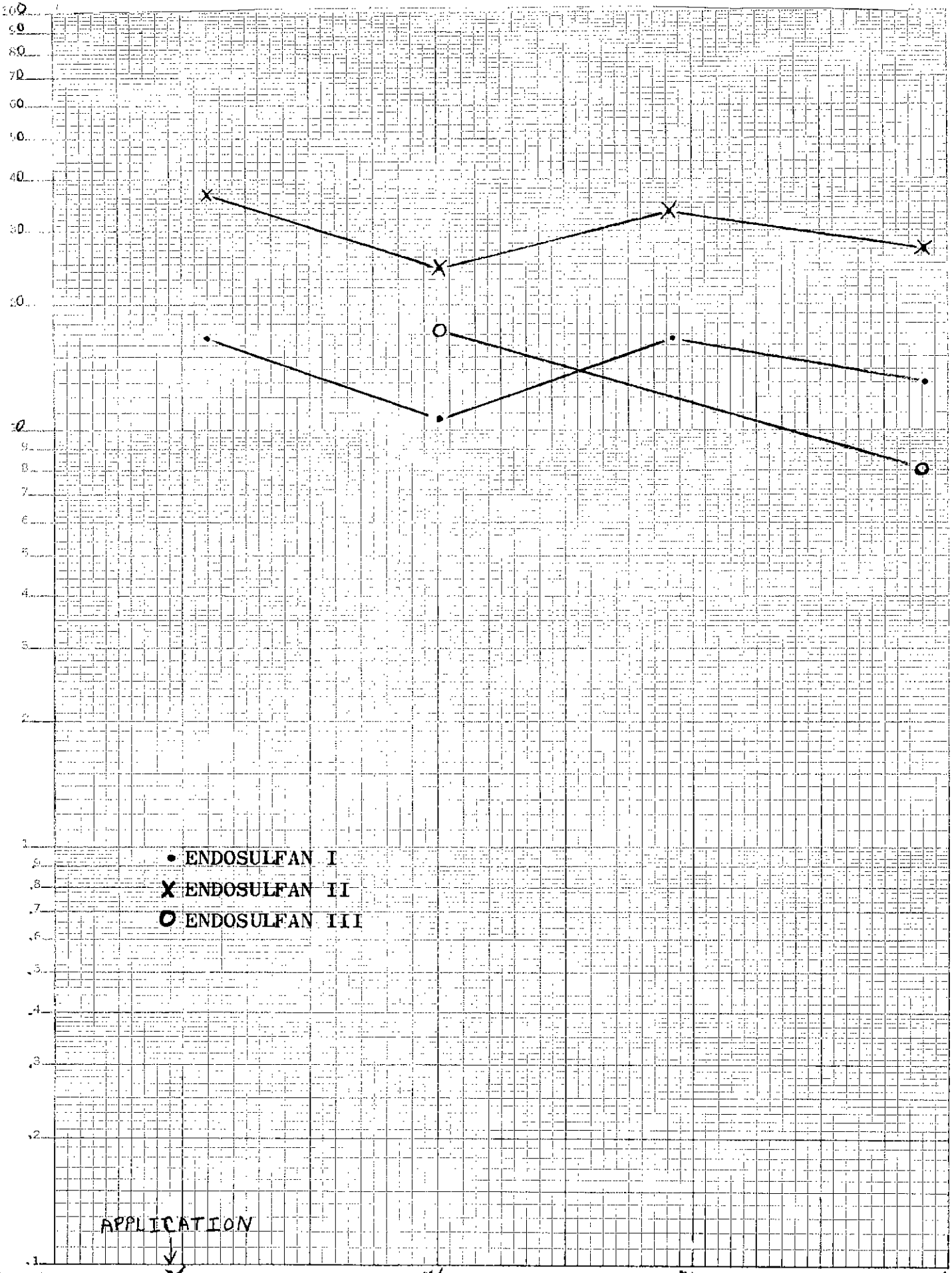
TOTAL ENDOSULFAN I, II, + III, RESIDUE (PPM)



Semi-Logarithmic
3 Cycles x 10 to the inch